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(54) Method for manufacturing ethylene
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Osaka-shi(74) Agent: Katsuya Kimura, Patent Attorney
(and 1 other)**Specifications****1. Title of Invention:**

Method for manufacturing ethylene polymer pellets with improved odor

2. Claims:

A method for manufacturing ethylene polymer pellets with improved odor, characterized in that, in a method for keeping ethylene polymer pellets resident in an odorless, inert gas flow at a temperature above 20°C and below the softening point of said ethylene polymer, the flow rate of the gas is less than 1000 m³/T·hr, the residence time is less than 240 hr, and the combination of the temperature, gas flow rate, and residence time satisfies the following condition:

$$t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) \geq 1.2 \times 10^{-8}$$

wherein: K: volatile ingredient reduction ratio = (volatile ingredient quantity in pellets after treatment)/(volatile ingredient quantity in pellets before treatment)

t: residence time (hr)

W: flow rate of gas per unit pellet weight (m³/T·hr)

T: temperature of gas flow ($^{\circ}\text{K}$)

R: gas constant = 1.987 cal/mol \cdot oK

3. Detailed Explanation of the Invention:

This invention concerns a method for manufacturing an ethylene polymer with improved odor.

Up to now, ethylene polymers, such as polyethylene, have been widely used as materials for packaging food products because of their excellent transparency, flexibility, and hygienic qualities. However, since the resins have characteristic odors, they have the drawback that these odors are transferred to the contents when they are used as packaging materials for food products, causing unpleasant feelings, and markedly harming the value of the product. It is desirable to reduce the odors of the packaging materials as much as possible, especially when they are used for packaging biscuits, milk products, teas, coffee, etc., to which these odors are especially easily transferred.

It is said that, in general, these odors are perceived when the volatile ingredients with molecular weights of about 300 or less are evaporated into the air by their own vapor pressure and their molecules stimulate the human olfactory cells.

Lubricating oils, solvents, additives, etc., are used in very small quantities in the manufacturing processes for ethylene polymer pellets, and since parts of the volatile ingredients among them remain in the molded products even after the pellets have been molded, odors are transferred to the contents of the food packaging materials made of these molded products and are deleterious to their commercial values.

Therefore, the odors of the molded products will be improved if the contents of the kinds of volatile ingredients which cause odors in the raw materials of the pellets are reduced at the raw material stage.

The inventors discovered that the odors of the pellets could be greatly improved by making the flow rate of the odorless, inert gas in which the ethylene polymer pellets flow less than $1000 \text{ m}^3/\text{T}\cdot\text{hr}$, at a temperature higher than 20°C and lower than the softening point of the ethylene polymer, and the residence time less than 240 hours, and by using a combination of the temperature, gas flow rate, and residence time which satisfies the formula given below.

That is, the purpose of this invention is to provide a method for manufacturing ethylene polymer pellets with improved odor, suitable for food wrapping materials.

The ethylene polymers used in this invention are not limited to ethylene homopolymers; these ethylene polymers may be manufactured by publicly known polymerization methods of the existing technologies even if they are copolymers containing other α -olefins, vinyl acetate, acrylates, etc., or blends of these.

The pellets in this invention can be made to reside in suitable vessels of a semi-sealed construction which have inlets and outlets for gas flows. Examples of these vessels are silos, hoppers, and tanks.

The temperature of the gas flow must be below the softening point of the ethylene polymer involved. If it is at or above the softening point, the pellets in the vessel will be fused by their own weight and will not be able to be expelled from the vessel, or they will cause operational problems.

Moreover, the diffusion of the volatile ingredients in the pellets will be slow at temperatures below 20°C, and the purpose of this invention will not be achieved to a sufficiently effective extent.

The odorless, inert gases used in this invention can be selected as desired from nitrogen, air, carbon dioxide, helium, etc.

The flow rate of the gas flow and the residence time are determined as follows.

The volatile ingredients in the pellets diffuse into the amorphous parts of the polymer and exude to the pellet surface. The exuded volatile ingredients transpire into the surrounding gas due to their own vapor pressures until an equilibrium with the atmosphere surrounding the pellets is reached.

The inventors discovered that the rate of diffusion in the pellets is governed by the temperature and that the rate of transpiration from the pellet surface is governed by the rate of exchange of the gas in the pellet atmosphere, in a semi-sealed system, that is, by the flow rate of the gas flow and the temperature. Hence, the total degassing rate of the volatile ingredients from the pellets follows the equation:

$$\log K = -5 \times 10^7 \cdot t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) \quad (1)$$

wherein: K: volatile ingredient reduction ratio = (volatile ingredient quantity in pellets after treatment)/(volatile ingredient quantity in pellets before treatment)

t: residence time (hr)

W: flow rate of gas per unit pellet weight ($\text{m}^3/\text{T} \cdot \text{hr}$)

T: temperature of gas flow ($^{\circ}\text{K}$)

R: gas constant = 1.987 cal/mol·ok

The relationship between the intensity of an odor and the concentration of the odiferous substance is said to be given approximately by the Weber-Fechner law: odor intensity • log (odiferous substance concentration); if the concentration of the odiferous substance is reduced to 1/4 of its original value or less, the odor can be perceived as being reduced.

Therefore, for the purpose of this invention, it is necessary that $K \leq 0.25$. Substituting this value in equation (1) gives formula (2):

$$t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) \geq 1.2 \times 10^{-8}. \quad (2)$$

Therefore, to achieve the purpose of this invention, the combination of the temperature, gas flow rate, and residence time must satisfy formula (2). From the point of view of economic efficiency, however, it is not practically significant for the gas flow rate to be higher than $1000 \text{ m}^3/\text{T} \cdot \text{hr}$ or the residence time to be longer than 240 hours.

This invention will be explained below by giving working examples.

Working Example 1

Two hundred grams of low-density polyethylene pellets (MI=2.0, density=0.924 g/cc) were put into a cylindrical vessel with a volume of 600 ml, with a gas inlet and outlet, and the pellets were kept in it for 20 hours, while air heated to 60°C was allowed to flow at a rate of 100 m³/T·hr per unit weight of the pellets.

When the left side of formula (2) was calculated under these treatment conditions, it became

$$t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) =$$

$$20 \exp [1.4 \times 10^{-3} \times 100 - 13400/(1.987 \times 333)] = 3.7 \times 10^{-8} > 1.2 \times 10^{-8},$$

and the specified condition was satisfied.

Working Example 2

Using the same material as in Working Example 1, the pellets were kept in the vessel for 100 hours, while air heated to 25°C was allowed to flow at a rate of 100 m³/T·hr per unit weight of the pellets.

When the left side of formula (2) was calculated under these treatment conditions, it became

$$t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) =$$

$$100 \exp [1.4 \times 10^{-3} \times 100 - 13400/(1.987 \times 298)] = 1.7 \times 10^{-8} > 1.2 \times 10^{-8},$$

and the specified condition was satisfied.

Comparison Example 1

Using the same material as in Working Example 1, the pellets were kept in the vessel for 20 hours, while air heated to 25°C was allowed to flow at a rate of 100 m³/T·hr per unit weight of the pellets.

When the left side of formula (2) was calculated under these treatment conditions, it became

$$t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) =$$

$$20 \exp (1.4 \times 10^{-3} \times 100 - [13400/(1.987 \times 298)]) = 0.34 \times 10^{-8} < 1.2 \times 10^{-8},$$

and the specified condition was not satisfied.

Working Example 3

Using the same material as in Working Example 1, the pellets were kept in the vessel for 6 hours, while air heated to 60°C was allowed to flow at a rate of 200 m³/T·hr per unit weight of the pellets.

When the left side of formula (2) was calculated under these treatment conditions, it became

$$t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) =$$

$$6 \exp (1.4 \times 10^{-3} \times 200 - [13400/(1.987 \times 333)]) = 1.3 \times 10^{-8} > 1.2 \times 10^{-8},$$

and the specified condition was satisfied.

Comparison Example 2

Using the same material as in Working Example 1, the pellets were kept in the vessel for 6 hours, while air heated to 60°C was allowed to flow at a rate of 20 m³/T·hr per unit weight of the pellets.

When the left side of formula (2) was calculated under these treatment conditions, it became

$$t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) =$$

$$6 \exp (1.4 \times 10^{-3} \times 20 - [13400/(1.987 \times 333)]) = 1.00 \times 10^{-8} < 1.2 \times 10^{-8},$$

and the specified condition was not satisfied.

Working Example 4

Two hundred grams of ethylene-vinyl acetate copolymer pellets (MI=2.0, density=0.93 g/cc, vinyl acetate content=5%) were treated by the same method as in Working Example 1 for 40 hours, while air heated to 40°C was allowed to flow at a rate of 100 m³/T·hr per unit weight of the pellets.

When the left side of formula (2) was calculated under these treatment conditions, it became

$$t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) =$$

$$40 \exp (1.4 \times 10^{-3} \times 100 - [13400/(1.987 \times 313)]) = 2.0 \times 10^{-8} > 1.2 \times 10^{-8},$$

and the specified condition was satisfied.

Comparison Example 3

Using the same material as in Working Example 4, the pellets were treated by the same method as in Working Example 1 for 10 hours, while air heated to 40°C was allowed to flow at a rate of 100 m³/T·hr per unit weight of the pellets.

When the left side of formula (2) was calculated under these treatment conditions, it became

$$t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) =$$

$$10 \exp (1.4 \times 10^{-3} \times 100 - [13400/(1.987 \times 313)]) = .5 \times 10^{-8} < 1.2 \times 10^{-8},$$

and the specified condition was not satisfied.

Table 1 shows the results of comparing the pellets treated under the conditions of Working Examples 1–4 and Comparison Examples 1–3 with untreated pellets of the same materials by a functional odor test.

From these results, the odors of the pellets are clearly improved when the combination of the treatment conditions satisfies formula (2).

Table 1

| Material | Working or Comparison Example No. | Treatment conditions | | | Odor (note) |
|-----------------------------------|-----------------------------------|----------------------|----------------------------------|---------------------|-------------|
| | | Temperature (°C) | Flow rate (m ³ /T·hr) | Residence time (hr) | |
| Low-density polyethylene | Untreated | | | | Bad |
| | Working Example 1 | 60 | 100 | 20 | Good |
| | " 2 | 25 | 100 | 100 | Good |
| | Comparison Example 1 | 25 | 100 | 20 | Bad |
| | Working Example 3 | 60 | 200 | 6 | Good |
| Ethylene-vinyl acetate co-polymer | Comparison Example 2 | 60 | 20 | 6 | Bad |
| | Untreated | | | | Bad |
| | Working Example 4 | 40 | 100 | 40 | Good |
| | Comparison Example 3 | 40 | 100 | 10 | Bad |

(Note) One hundred grams of the pellets of each material were put into an Erlenmeyer flask; the flask was sealed and heated at 100°C for one hour, after which it was cooled to room temperature. The treated and untreated pellets were compared pairwise by a panel of 10 persons; the pellets which were judged to have been improved in their odors, compared with the untreated pellets, by more than half of the panel members, were considered to be good ones.

Amendments (Spontaneous)

April 5, 1978

To: Zenji Kumagai, Commissioner of Patents

1. Index of Case:

Patent Application No. 52-118433

2. Title of Invention:

Method for manufacturing ethylene polymer pellets with improved odor

3. Person Making Amendments:

Relationship to Case: Applicant

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Representative: Takeshi Hijikata

4. Agent:

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5. Object of Amendments:

Claims and Detailed Explanation of Invention of Specifications

6. Content of Amendments:

The Claims and the Detailed Explanation of Invention of the Specifications are amended as follows:

- (1) The Claims are amended as shown on the attached sheet.
- (2) Line 2, p. 6 of Specifications: "oK" is amended to "°K".

Claims:

A method for manufacturing ethylene polymer pellets with improved odor, characterized in that, in a method for keeping ethylene polymer pellets resident in an odorless, inert gas flow at a temperature above 20°C and below the softening point of said ethylene polymer, the flow rate of the gas is less than 1000 m³/T·hr, the residence time is less than 240 hr, and the combination of the temperature, gas flow rate, and residence time satisfies the following condition:

$$t \cdot \exp (1.4 \times 10^{-3} W - 13400/RT) \geq 1.2 \times 10^{-8}$$

wherein: t: residence time (hr)

W: flow rate of gas per unit pellet weight (m³/T·hr)

T: temperature of gas flow (°K)

R: gas constant = 1.987 cal/mol·°K